

## ***KINETICS OF DELIQUESCENCE***

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### **ABSTRACT**

We examine deliquescence phase transformation for inorganic salt particles ranging from bulk down to several nanometers in size. Thermodynamic properties of the particles, coated with aqueous solution layers of varying thickness and surrounded by vapor, are analyzed. A thin layer criterion is introduced to define a limiting deliquescence relative humidity (DRH). Nano-size particles are predicted to deliquesce at relative humidity just below the DRH on crossing a nucleation barrier, located at a critical solution layer thickness. This barrier vanishes precisely at the DRH defined by the criterion. For a population of particles, the inherent random nature of the nucleation process is predicted to result in a distribution of RH values over which deliquescence will be seen to occur. Measurement of this (apparent) non-abrupt deliquescence of the population should provide both a validation of the nucleation mechanism and a quantitative determination of nucleation rate. This paper presents calculations of crossing (i.e. deliquescence) rate using the theory of mean first passage times (MFPT). MFPT theory is shown to provide a generalization of Becker-Döring nucleation kinetics especially useful for barrier heights much lower than those typically encountered in vapor-liquid nucleation. Barrier heights for deliquescence depend on the concentration of pre-deliquesced particles and observation time, but are typically in the 5-15kT range. Calculations use the tandem nano-differential mobility analyzer setup of Biskos et al. [1] as a model framework. In their experiment, a concentration of dry salt particles is subject to a higher RH for some observation time, after which is measured the (well-separated) populations of un-deliquesced particles and those that have deliquesced. Theoretical estimates for the conversion kinetics are presented as a function of dry particle size, DRH, and salt properties.

1. G. Biskos, A. Malinowski, L. M. Russell, P. R. Buseck, and S. T. Martin, *Aerosol Sci. and Technol.* **40**, 97 (2006).

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